content of the soil is high. In these regions, the boron content of water used for irrigation is sometimes great enough to cause injury to crops.

Carl S. Scofield and L. V. Wilcox, of the Department of Agriculture, found that 0.5 p.p.m. of boron in irrigation water injured some crops. A boron content of 1.0 p.p.m. caused injury to most crops, even those with high boron requirements.

The boron that occurs in injurious concentrations in irrigation water may be derived from the solution of exposed outcrops of soluble boron minerals, from underground waters, or directly from volcanic gases dissolved in percolating waters. The areas in which boron toxicity may occur are not large; nevertheless, the injury to crops in some of these areas is serious. These areas are located primarily in southern California, western Nevada, and parts of Arizona.

Certain control measures are available for eliminating or preventing the accumulation of toxic concentrations of boron in soils. Thorough leaching of contaminated soils is usually recommended when possible. Mixing irrigation water high in boron content with water low in boron content is recommended as a method of utilizing all the water available for irrigation without building up toxic concentrations.

Borax, or other boron fertilizers, therefore must not be used indiscriminately. The effect may be disastrous. Fortunately, the effect in humid regions is temporary; the boron soon leaches from the soil. In the absence of official recommendations, farmers should use borax at the rate of only a few pounds to the acre and only on small areas until experience shows the need for boron and the proper amount to use.

Boron fertilization is becoming a necessary and accepted practice in many areas of the United States, just as plastic is becoming more widely used in the kitchen. But just as the housewife knows that plastic has its limitations, the farmer knows that the use of boron has its limitations.

# Copper and Soil Fertility

Walter Reuther

**Soils high in organic matter and weathered, sandy soils are likely to be deficient in copper. A great deficiency may cause serious stunting of growth and visible symptoms of disease in plants, but moderate deficiency may merely reduce yields.**

Copper once was regarded as a plant poison, as indeed it may be when too much of it is used on soil. As a matter of fact, a 5-percent solution of copper sulfate was one of the first spray formulations used for the chemical control of weeds. Concentrations of 0.1 percent to 0.2 percent of copper in the form of water suspensions of insoluble hydroxides, carbonates, or oxides are an effective fungicide. Research workers noted long ago that solutions containing as little as 1 part per million of soluble copper killed algae and fungus spores.

Bordeaux mixture, the first widely used fungicide applied to foliage by spraying, is prepared by dissolving 5 to 10 pounds of copper sulfate in 100 gallons of water and adding approximately an equal weight of lime (calcium hydroxide) or soda ash (sodium carbonate).

Many researchers before 1927 observed that Bordeaux sprays sometimes had stimulating effects on vigor and yield that were not associated with the control of fungus diseases. Other research workers noted that minute amounts of copper were distributed through all plant tissues. Some thought that the stimulating effects of small amounts of copper on plants and fungi were due to some indirect action of copper or to "an irritation response." Others thought that copper might be an essential element in the metabolism of plants and animals.

The first credible evidence that copper was an essential element in the nutrition of lower plants was provided by H. Bortels, a German scientist, in 1927. He showed that a deficiency of copper in the culture medium of the common bread mold, *Aspergillus niger*, reduced growth by 50 percent and changed the color of the spores from black to brown. The addition of minute amounts of copper to the cultures produced normal growth and black spores.

Confirmation of his results was soon provided by other scientists, who discovered that copper is essential for the normal growth of a wide variety of fungi and yeasts and also of green plants and animals. R. V. Allison and his associates in 1927 showed that the almost complete failure of many crops to grow on the peat soils of the Florida Everglades could be cured by fertilization with copper. They postulated that the disorder was due to a lack of sufficient copper for normal plant growth.

THE SYMPTOMS of copper deficiency in green plants vary considerably with species and perhaps other complicating factors. No general description of visual copper deficiency symptoms can therefore be made.

Crops showing a moderate response in vigor and yield to applications of copper to soil may not exhibit striking symptoms of disease other than lack of normal vigor. Usually some parts of fields or orchards in which moderate responses to copper are obtained have a few plants that show acute pathological symptoms of copper deficiency.

Symptoms of copper deficiency of citrus were among the first to be recognized as such in the field and are fairly typical of symptoms on other tree crops. Primary symptoms of the disease are gum pockets under the bark, stained spots on the bark of terminal twigs and defoliation on them, the formation of multiple buds in the leaf axils and shortening of internodes, a dying back of the twigs, and a characteristic staining of the fruit because of the formation of gum-soaked areas in the rind. Affected fruits frequently split open and drop before they attain full size. In Florida, where it was first noted and described, the disease was known as exanthema, dieback, or ammoniation. The last term indicates that growers recognized that it was associated with heavy applications of "ammonia" (nitrogen) fertilizers.

Copper deficiencies of other tree crops have been reported in other sections of the United States and the world. Usually shoots die back and the foliage may show marginal or spotted necrosis and chlorosis. Multiple bud formation, rosetting (shortening of shoot internodes), malformation of leaves, and an excessive gumming also may occur.

A disease of grains called white tip, yellow tip, or reclamation disease has been reported in various parts of the world. It responds to copper fertilization. It is characterized by a necrosis of the tips of older leaves and a marginal chlorosis of the tips of younger leaves, which may remain unrolled and tend to wilt readily. The heads may be dwarfed and distorted. Grain production may be reduced more than the vegetative growth.

Symptoms of copper deficiency have been described for sugarcane, a number of vegetable crops, peanuts, and other plants.

THE FUNCTIONS OF COPPER in the mineral nutrition of plants appear to be numerous, varied, and complex. In fact, none of the essential nutrient elements has a single, simple job in the economy of plant growth and development. Copper is no exception, although evidence concerning many of its functions is quite meager.

Copper seems to be concentrated more in the rootlets of plants than in leaves or other tissues—it may there-

406157°—57——10

fore have an important function in root metabolism.

Analyses of the tissues in a copper-deficient plant indicate it to be abnormally high in proteins and amino acids, although similar effects have been noted with several other deficiencies of essential plant nutrients.

Heavy fertilization with nitrogen tends to increase the severity of pathological symptoms of copper deficiency. Plants supplied with ammonium nitrogen in culture solutions respond favorably to higher levels of copper than do plants supplied only with nitrate nitrogen, an indication that copper is related somehow to utilization of ammonium nitrogen by plants. All the evidence suggests that copper is important in the utilization of proteins in the growth processes of plants.

The rate of photosynthesis of leaves on copper-deficient plants is abnormally low. The concentration of copper in chloroplasts (minute corpuscle-like bodies in plant cells in which the green pigment chlorophyll is concentrated) is larger than in the leaf as a whole. We have evidence that copper is involved in oxidation-reduction reactions in plants.

Copper probably functions as an enzyme activator or as an integral part of enzyme molecules involved in certain reactions. For example, potatoes grown in the Netherlands on soil that is low in available potassium but has adequate copper tend to blacken in storage because of the oxidation of tyrosine (and related phenolic compounds) by the enzyme tyrosinase to the black pigment, melanin.

On the other hand, potatoes grown on soil low in potash and low in copper have a high content of tyrosine (as do potatoes grown in low-potash and high-copper soil) but have much less tendency to produce blackening of cut surfaces. Potatoes grown on low-copper soil exhibit less than one-tenth of the tyrosinase activity of potatoes grown on normal copper soil. The black pigment, melanin, is probably like that produced in the spores of *Aspergillus niger* and inhibited in production in spores of that organism when grown when copper is deficient.

Plants suffering from copper deficiency are low in ascorbic acid oxidase activity. Other enzymes that appear to involve copper are cytochrome C and laccase.

Because of its inherent physical and chemical properties, copper forms a vast array of compounds with proteins, amino acids, and other organic compounds that commonly occur in the juices of plants and animals.

Two groups of such copper compounds, known as complexes and chelates, are probably of particular significance in the special functions that copper performs in the life processes of plants and animals. In complexes, because of its special properties, copper is held securely by a number of single chemical bonds to other atoms in molecules of proteins, amino acids, and related species of compounds. Chelates are similar to complexes, except that copper is held with tremendous security by extremely strong multiple chemical bonds.

The copper content of tissues of plants suffering from copper deficiency is abnormally low.

Among the tree crops, copper concentration in tissues of citrus has perhaps been the most extensively studied in various parts of the world. If copper in citrus leaves falls below about 4 p.p.m. (parts per million) in dry matter, severe copper deficiency symptoms are almost certain to be observed. In the range of about 4 to 5 p.p.m., mild to moderate deficiency symptoms may occur. Copper deficiency rarely occurs when the copper concentration in leaves is 6 p.p.m. or more. A copper concentration above 16 p.p.m. in normal citrus foliage is uncommon, unless contamination from foliage sprays is responsible.

About the same relationship between copper concentration in leaves and incidence of deficiency symptoms has been noted in a large number of other tree crops and many vegetable and agronomic crops.

Analyses of fibrous roots of citrus indicate that copper concentration in them may be about 5 to 10 times the concentration found in the leaves of the same trees, but we are not sure how the concentration of copper in roots of plants is related to copper deficiency.

Small grains that suffer severe copper deficiency (severe stunting, necrosis of foliage, distorted heads) may contain a normal concentration of copper in the aboveground tissues.

F. Steenbjerg found that in Denmark fertilization of such plants with a small amount of copper sulfate actually reduced copper concentration in tissues while at the same time it increased growth and yield considerably. Heavy fertilization with copper restored normal yield and growth and increased copper concentration in the tissues. This type of irregular relationship of concentration in tissues, incidence of deficiency symptoms, and response to copper fertilization, however, is the exception rather than the rule.

THE COPPER CONTENT of soils, according to limited analyses, varies quite widely.

Most mineral soils that have a texture between loam and clay have a total content of native copper of 10 to 200 p.p.m.—usually 25 to 60 p.p.m.

Very sandy soils, such as are common in the Atlantic Coastal Plains, contain 1 to 30 p.p.m. of native total copper, with most between 3 and 15 p.p.m.

Organic soils contain about the same range of native total copper as mineral soils. As a rule, the subsoil (B horizon) may contain somewhat less copper than the topsoil (A horizon). In some soils, the total copper does not vary significantly with depth. In others, the subsoil may contain significantly more copper than the topsoil.

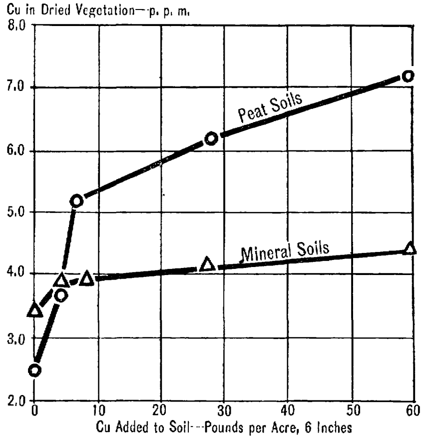
No good chemical method has been developed for assaying the amount of copper in soil available to plants. Rough correlations have been found between the copper removed by several soil extractants (acid or salt solutions) and the copper content of plants growing thereon or to response to copper fertilization. Such relationships are rule of thumb, and their use to determine needs often is limited to a small range of soil types and plant species.

Probably the most reliable—but not infallible—index of the copper status of soil with respect to a particular crop is the copper content of the foliage of the crop growing on it.

IN FLORIDA, I and my coworkers found that copper extractable by strong acid digestion of soil correlated reasonably well with the copper content of the tissues of plants grown on it. No doubt "wet ashing" soil with strong oxidizing chemicals liberates all the copper associated with the organic matter fraction of the soil, and subsequent extraction with more dilute acid displaces that held by exchange or other reactions on the surface of the clay, but leaves intact most of the copper within the crystal lattice of clay particles. Oxidation of Florida soils (containing 95 to 98 percent of sand) with concentrated nitric and sulfuric acids and digestion of the residue with dilute sulfuric acid brought more than 90 percent of the total copper content of the soil into solution.

A biological method of estimating availability of copper in soils has been widely used and appears to be fairly reliable. A specially prepared copper-free nutrient solution is inoculated with spores of the common bread mold, *Aspergillus niger*, a small amount of the soil to be assayed is added, and the culture is incubated for several days. The spore color developed is compared with a series of standards to estimate micrograms of available copper. Black spores indicate adequate available copper, and progressive shades of lighter color indicate increasing degrees of copper deficiency.

THE REACTIONS of copper with soil are not so clearly understood as are those of other essential elements.




*1. The relationship of copper content of pastures and forage crops to the application of copper sulfate to soils in Sweden.*

Some copper may be held by the colloidal fraction of the soil in much the same way as base elements, such as calcium or magnesium. A major part of copper, however, evidently is fixed with a degree of security such that it cannot be displaced readily by other common soil cations (such as calcium, magnesium, or potassium) in the ordinary range of soil acidity.

For example, scientists in Florida found that a normal NaCl (common table salt) solution at pH 6.0 would displace less than 5 percent of copper added to sandy soil at the rate of 100 pounds of copper to the acre and that most such soils could fix about three times as much added copper as ammonia ion. A high proportion of copper added to hydrogen or calcium-saturated clay was held in nonexchangeable form; that is, it could not be "exchanged" or displaced and leached out readily by solutions of other cations commonly found in soils and fertilizers.

Soil holds copper most securely in the range from pH 7 to 8, appreciably less securely at pH 6, and progressively less securely as the soil becomes more acid. In addition, the kind of minerals present in the clay fraction may influence the reaction of copper with soils.

Because of these reactions of copper with soil, a high proportion of copper added to soil as a fertilizer or fungicide residue is fixed rather permanently in the top few inches of the soil, unless the soil is very acid or cultivated deeply. This tight fixation may be due to the formation of complexes and chelates of copper with ligno-proteins and other humate compounds in soil organic matter and to a lesser extent to some analogous complexes with clay.

Thus organic matter, the kind and amount of clay minerals, and acidity are all major factors affecting the availability of copper in soils.

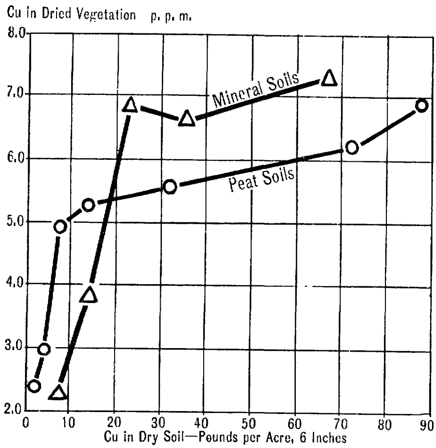
Copper fertilization of most soils deficient in copper usually produces a satisfactory crop response.

On mineral soils, a single application of 5 to 25 pounds of copper sulfate (bluestone) an acre usually is enough to correct the deficiency with pasture and field crops.

For organic soils, 50 to 200 pounds of copper sulfate an acre may be required for normal yields of vegetable and field crops. Other soluble salts, such as copper chloride or nitrate, have been used with results equal to copper sulfate. Insoluble oxides of copper and various copper ores also have been used. They may be quite effective if the rates are adjusted for copper content and the materials are finely divided.

In the sandy soils used for citrus orchards in Florida, annual applications of 15 to 50 pounds of copper sulfate an acre formerly were recommended for the control of ammoniation (copper deficiency) of citrus. In time, however, this practice led to toxic accumulations.

It is now recommended that a total of 50 to 100 pounds an acre of copper sulfate be added over a period of years to newly planted citrus orchards on virgin soil prone to be copper deficient. It is applied as an ingredient of mixed fertilizer (usually about 30 pounds of copper sulfate or the equivalent per ton) in several applications a year for 5 to 6 years before the trees begin heavy bearing. No further copper is recom-




*2. The relationship of copper content of pastures and forage crops to the copper content (perchloric acid extractable) of soils in Sweden.*

mended until indications of deficiency are again apparent.

On the muck soils of Michigan, farmers are advised to apply to responsive crops initial applications of 100 pounds an acre of copper sulfate and continue smaller annual applications until a total of about 250 pounds an acre has been applied. This provides enough residual available copper for many years.

Copper-deficient plants usually respond quickly and satisfactorily to foliage sprays of such copper compounds as Bordeaux mixture. Foliage sprays are often valuable emergency treatments when symptoms of copper deficiency are first observed. Soil applications usually are the most practical way of supplying the copper requirements of plants unless copper sprays are required routinely for the control of disease.

It was found in nearly all instances studied that single applications of copper to the soil produce strong residual effects, which may persist for many years. This is because copper is held tightly by the soil, it is not subject to leaching out of the main root zone, and the amount removed when a crop is harvested is small compared to the amounts usually applied. For example, about 30 years of heavy cropping are required to remove 1 pound of copper from an acre of citrus in the fruit.

As TO ANIMALS, it is generally recognized that the blood of those that suffer from copper deficiency is low in hemoglobin—that is, they have a type of anemia. Copper is not a part of the hemoglobin molecule, but it seems to be essential for the formation of hemoglobin. Other symptoms of copper deficiency in animals are retardation of growth, failure to fatten, coarsening and depigmentation of hair, poor reproduction, diarrhea, abnormalities of bone formation, nervous disorders, and general weakness. Incipient copper deficiency may first show up as a reduction in reproductive efficiency.

THAT TOXIC LEVELS of copper in the soil or nutrient solution can cause reduced growth, chlorosis of the foliage, and abnormal, stunted root development of such plants as corn, beans, and squash was demonstrated in 1917 by Dr. R. H. Forbes, of the University of California.

His analyses indicated that copper-stunted plants contained somewhat more copper in the foliage and much more copper in the roots than healthy plants. He concluded that the abnormally high concentration of copper in injured roots was combined largely with proteins and localized mainly inside the root in the promeristem and central stele and not in the outer epidermal or cortical tissues.

Later studies have disclosed that toxic amounts of copper in the soil or nutrient medium may reduce growth, depress the iron concentration in leaves, and cause symptoms of iron chlorosis. Copper toxicity also may interfere with the uptake of certain other heavy metals and phosphorus and otherwise derange the normal process of nutrient accumulation by roots. This is associated with stunting, reduced branching, and thickening and abnormal dark coloration of rootlets.

Somewhat similar toxic effects can be produced by other heavy metals, such as nickel, cobalt, zinc, and manganese. Nickel is appreciably more toxic than copper. Cobalt is slightly less toxic. Zinc and manganese are about one-tenth and one-thirtieth as toxic, respectively.

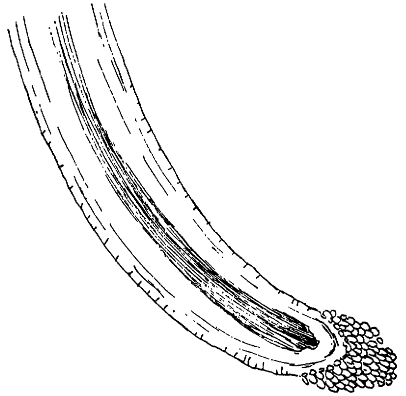
Instances of toxic concentration of copper developing in agricultural soils as a result of accumulation in many years of residual copper from the Bordeaux fungicides or from copper sulfate fertilization have been reported in Florida and France.

Toxic effects of high copper in citrus orchard soils in Florida are manifested in severe cases by a marked reduction in tree vigor and yield, severe chlorosis of foliage, and dieback of the twigs. Similarly, copper toxicity symptoms of several crops have been reported in some old vegetable fields having a large amount (more than 400 p.p.m.) of copper in the topsoil, the result of many years of frequent spraying of celery with Bordeaux mixture to control fungus diseases.

The chlorotic foliage of affected citrus trees in Florida has an abnormally low iron content, and the sparse, dark, stubby fibrous roots in the topsoil have an exceedingly high copper content. Such copper toxicity symptoms of citrus in most instances are associated with an acid soil condition (pH 4.0 to 5.5) produced by application of acid-forming fertilizers and large residues of sulfur used to control pests.

If the copper level in the soil is not too high, normal vigor of affected trees can be restored by applying one-fourth to one-half pound of chelated iron (iron ethylenediamine tetraacetate, or Fe-EDTA) per tree and sufficient lime or soda ash to raise the pH of the topsoil to about pH 7. The iron chelate quickly corrects the chlorosis by supplying iron to the top—presumably mainly through the healthy roots in the subsoil, which are not affected by copper toxicity. The heavy liming usually reduces the availability of copper enough to permit the gradual restoration of normal rooting in the topsoil.

Studies with pots of virgin Florida



*3. The tip of a corn root that is exposed to a toxic concentration of copper. The dark part indicates that copper is localized in the inner promeristem and central stele portion of the root.*

orchard topsoils containing about 5 p.p.m. or less of total copper indicate that the addition of 10 to 25 p.p.m. of copper may benefit citrus seedlings, and additions of 50 to 200 p.p.m. may reduce growth and cause chlorosis. The degree of toxicity obtained is controlled largely by the exchange capacity (related primarily to the organic matter content) and degree of acidity of these very sandy soils.

We have evidence also that a high phosphate content of soils reduces copper toxicity, as judged by total growth of seedlings in pots. Paradoxically, high phosphorus may increase the incidence of chlorosis symptoms on such soils.

Field studies of acid, sandy soils in citrus orchards in Florida indicate that slight toxic effects in the trees may occur when the copper level in the soil reaches about 1.6 milliequivalents of copper per milliequivalent of exchange capacity in 100 grams of dry soil. At twice this concentration, mild to severe toxic effects are likely to be observed. In other words, the lower the clay and organic matter content of a soil, the lower is the amount of added copper required to produce toxicity.

Scientists in France found that copper accumulated over many years in acid soils from residues of Bordeaux sprays in vineyards may be toxic to a variety of crops. Pot tests indicated that addition of about 200 p.p.m. of copper from copper sulfate produced a toxic reaction in soils low in copper, but otherwise comparable to Alsatian vineyard soils, which were found to contain as much as 400 p.p.m. of copper. Among the crops tested, vines were most resistant to copper toxicity; clover and alfalfa were most sensitive.

Symptoms of copper poisoning were found in southern France in spinach and gladiolus grown in a field once occupied by a peach orchard that had been sprayed heavily for many years with Bordeaux mixture. Only the parts of the field having quite acid soil (pH 4.5 to 4.7) were affected; the copper content of that soil was 98 to 130 p.p.m.

Future research in disease control and soil fertility with copper-containing compounds should evaluate the residual effects, because nearly all the copper applied to crops will normally be fixed in the few inches near the surface of the soil.

# Manganese and Soil Fertility

G. Donald Sherman

**Plants require tiny amounts of manganese to grow and mature properly. Otherwise they fail as completely as if they lacked the major elements.**

Paul M. Harmer, in research work at Michigan Agricultural Experiment Station, reported a 100-bushel increase an acre in yields of potatoes after the manganese-deficient soil in which they were growing received a liberal application of manganese sulfate. He obtained an increase of 561 bushels of potatoes an acre after he had applied a small amount of manganese sulfate in Bordeaux sprays.

Cereal crops grown on manganese-deficient soils often fail to yield enough to replant the field. The cereals need less manganese than alfalfa does. Peppermint, spearmint, and rhubarb grow normally on a soil in Michigan that had too little manganese for onions, potatoes, alfalfa, oats, and beans.

Manganese-deficient soils have been found in many parts of America.

Chemical analyses have disclosed that the manganese content of plants of the same crop vary greatly.

Manganese with the aid of iron assists in the synthesis of chlorophyll, since all chlorophyll tissues have the highest concentrations of manganese.

In research with field peas in Michigan, I found that manganese controls the state of oxidation of several oxidation-reduction systems in the plant. Conditions existed in manganese-deficient plants that favored the oxidation of iron, ascorbic acid, and glutathione to their respective oxidized forms. In a normal plant these constituents occur in their reduced form.

The staining of iron in plant tissue showed the deposition of ferric iron, an insoluble form of iron, in the veins of pea leaves of a manganese-deficient plant, whereas the normal plant gave no test for ferric iron in the veins of the leaves. The normal leaf had an even distribution of ferrous iron, an available and active form of iron, throughout the leaf tissue; the manganese-deficient leaf showed only small amounts of ferrous iron in tissue near the veins. Recalling the pattern of the chlorosis (yellowing) developed on pea leaves, the results showed an almost complete absence of iron in the chlorotic, yellow parts of the leaf. The manganese-deficient leaves contained more iron, which supports the function of manganese in the movement of iron in plants.

Symptoms of a deficiency of manganese have been established for most of the agronomic and horticultural crops by growing the plants in purified cul-